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(54) NICKEL ELECTRODE FOR ALKALINE STORAGE BATTERY AND ALKALINE STORAGE BATTERY USING THIS NICKEL ELECTRODE

(57)Abstract:

PURPOSE: To provide a nickel electrode for an alkaline storage battery and an alkaline storage battery using this nickel electrode by preventing the electrode from swelling with a long life further with charging efficiency excellent at a high temperature.

CONSTITUTION: Zinc, magnesium and cobalt are contained in a solid solution condition in nickel hydroxide powder which is a main active material of a positive electrode, and further this nickel hydroxide powder is coated with a compound of zinc, magnesium, lead, indium, silver, copper, lanthanum or scandium. A nickel electrode for an alkaline storage battery is combined with an alkaline electrolyte of adding 1mol/liter or less lithium hydroxide to this electrode.

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CLAIMS

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[Claim(s)]

[Claim 1] The nickel electrode for alkaline batteries characterized by having contained zinc, magnesium, and cobalt in the state of dissolution to the nickel hydroxide powder which is the main active material of a positive electrode, and covering this nickel hydroxide powder with zinc, magnesium, lead, an indium, silver, copper, a lanthanum, or the compound of a scandium.

[Claim 2] The nickel electrode for alkaline batteries according to claim 1 whose content of cobalt the shape of particle has the spherical internal pore volume of the aforementioned nickel hydroxide powder at 0.1 or less ml/g, and is 5 % of the weight or more.

[Claim 3] The nickel electrode for alkaline batteries according to claim 1 whose compound which covers said nickel hydroxide powder is a hydroxide or an oxide and the amount of covering of whose is 1 - 8 % of the weight to nickel hydroxide.

[Claim 4] A nickel electrode according to claim 1 and one mol/l. Alkaline battery characterized by using combining the alkali electrolytic solution which added the following lithium hydroxides.

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DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the alkaline battery using the nickel electrode for alkaline batteries and this which are used for a nickel cadmium battery, a nickel metal hydride battery, etc.

[0002]

[Description of the Prior Art] Although the nickel cadmium battery and the nickel metal hydride cell are broadly used as pocket power sources, such as a portable electronics device, the actuation ambient atmosphere of the cell used in these devices with the formation of small lightweight of these devices every year, containing tends to serve as an elevated temperature. For this reason, amelioration of the elevated-temperature property of these cells, especially improvement in charging efficiency are demanded strongly. Moreover, although these cells attract attention as a power source for electric vehicles in recent years, since cell ambient temperature becomes 60-degree-C order, the improvement in the charging efficiency at the time of an elevated temperature is indispensable [ an operating environment is transit and parking in the flame world, and ].

[0003] Conventionally, in order to control the oxygen evolution reaction which competes with oxidation reaction of a nickel hydroxide electrode, the decomposition potential of the electrolytic solution is raised to improvement in the charging efficiency at the time of the elevated temperature of a cell, or raising the oxygen overvoltage of the nickel electrode itself is performed to it. The approach of specifically adding a high-concentration lithium hydroxide in the potassium-hydroxide water solution which is \*\* electrolytic solution, the approach of carrying out solid-solution addition of the cobalt at the nickel hydroxide which is \*\* main active material, the approach of covering the front face of \*\* nickel hydroxide with cadmium hydroxide, etc. are performed.

[0004] However, the approach of \*\* had a limitation in acquiring the charging efficiency which was moreover excellent only in this approach in the elevated-temperature field 40 degrees C or more with the fall of increase and a low-temperature high-rate-discharge property, degradation of capacity, disappearance of the surface smoothness of an electrical potential difference, etc. in resistance of the electrolytic solution. \*\* Although an approach enables improvement in thermophilic ability by carrying out abundant addition of the cobalt, it produces reduction of the capacity per unit weight of an active material, the fall of the life by electrode swelling, etc. Moreover, although the approach of \*\* makes oxygen evolution potential \*\* and raised the oxygen overvoltage, cadmium had possibility of it having been eluted in part, having deposited in a negative electrode, and producing a short circuit, in the electrolytic solution at the time of elevated-temperature charge, and there was a limitation in acquiring the charging efficiency which was excellent in the elevated-temperature field 40 degrees C or more only by this approach like \*\*. Thus, there is a trouble in the conventional approach and it has fully come to satisfy an above-mentioned demand.

[0005]

[Problem(s) to be Solved by the Invention] This invention is made in view of the above-mentioned trouble, and offers the alkaline battery using the nickel electrode for the alkaline batteries which were excellent in the charging efficiency at the time of an elevated temperature, without being long lasting and decreasing the energy density of an electrode which prevented electrode swelling, and this electrode.

[0006]

[Means for Solving the Problem] The nickel electrode of this invention as nickel hydroxide powder which is the main active material Zinc, magnesium, and cobalt are contained in the state of dissolution. A nickel hydroxide particle Zinc, It is characterized by using the powder which carried out surface coating with magnesium, lead, an indium, silver, copper, the lanthanum, or the compound of a scandium. As for a nickel hydroxide particle, it is desirable for internal pore volume to be a spherical gestalt in 0.1 or less ml/g, the cobalt content of nickel hydroxide powder is 5 – 10 % of the weight, and, as for the amount of covering of said compound, it is desirable that it is 1 – 8 % of the weight to nickel hydroxide. Moreover, the alkaline battery of this invention is the above-mentioned nickel electrode and one mol/l. It is characterized by consisting of the alkali electrolytic solution which added the following lithium hydroxides.

[0007]

[Function] The charging efficiency of a nickel electrode improves by controlling the oxygen evolution reaction (decomposition reaction of the electrolytic solution) which is a competitive reaction. Control of this oxygen evolution reaction is attained by making oxidation potential of a nickel hydroxide active material into \*\*, making oxygen evolution potential \*\* more, and enlarging more an oxygen overvoltage (difference of oxygen evolution potential and oxidation potential). Solid-solution addition of the cobalt to nickel hydroxide has the operation which makes oxidation potential of a nickel electrode \*\* in proportion to the amount. Moreover, by carrying out solid-solution addition of zinc and the magnesium at coincidence, generation of gamma-NiOOH which caused the swelling of a nickel electrode is prevented, and reinforcement is made possible. This operation does not exist at independent addition of cobalt. Moreover, the fall of the energy density of the electrode by the capacity reduction per unit weight of the active material by abundant addition of cobalt becomes possible [ preventing by raising the tap density of the powder itself, making internal pore volume of nickel hydroxide powder smaller than the powder of the conventional process, and it carrying out densification, and using the configuration as spherical ].

[0008] On the other hand, although generated also with the zinc which carried out solid-solution addition, it becomes possible to make it carry out more effectively of the shift to \*\* of oxygen evolution potential by covering zinc, magnesium, lead, an indium, silver, copper, a lanthanum, or the compound of a scandium on the front face of the nickel hydroxide particle which is the place of an oxygen evolution reaction. When this element is zinc, magnesium, lead, a lanthanum, an indium, or a scandium, even if the compound covered even if dissolves in part into the electrolytic solution especially, it does not deposit as a metal, it deposits in a negative electrode like [ in cadmium hydroxide covering of a conventional method ], and may stop producing a short circuit etc. in the charge and discharge potential of a cadmium electrode metallurgy group hydride electrode. Moreover, it becomes possible to constitute the alkaline battery which was further excellent in the charging efficiency at the time of an elevated temperature, and a discharge property with combination with the addition to the electrolytic solution of the low-concentration lithium hydroxide of the range without degradation of application to the nickel electrode of an active material with the high oxygen overvoltage of this invention, the surface smoothness of an electrical potential difference, or the discharge property at the time of low temperature.

[0009] Thus, this invention makes it possible to obtain the pollution-free nickel electrode which controlled electrode swelling while it increases notably the potential difference of the oxidation potential of a nickel electrode, and oxygen evolution potential and raises the charging efficiency at the time of an elevated temperature.

[0010]

[Example] Detail of the example of this invention is given below. Having added the ammonium sulfate, having considered as the ammine complex, and controlling alkalinity to pH 11–13, the nickel hydroxide powder of this invention was dropped agitating a sodium–hydroxide water solution violently, and the water solution which added the specified quantity of a zinc sulfate or magnesium sulfate, and cobalt sulfate to the nickel sulfate was made to carry out deposit growth, and it produced in it various kinds of nickel hydroxide particles from which the content of zinc, magnesium, and cobalt differs. The content of zinc, magnesium, and cobalt was prepared in 0 – 8 % of the weight, and 0 – 10% of the weight of the range, respectively. The internal pore volume of 0.02–0.09ml [ g ] /and the gestalt of those which measured the tap density of the obtained nickel hydroxide powder with about 2g [ ml ] /and a nitrogen adsorption process was spherical, and was powder high-density about 20% as compared with the powder (tap density is 1.6g/ml, and internal pore volume is 0.14ml/g) produced with the well-known conventional method.

[0011] It was immersed in the sodium–hydroxide water solution, and these powder was used as the hydroxide, after being immersed in water solutions, such as a zinc sulfate of a constant rate, a cadmium sulfate, and a copper sulfate, and the front face of a nickel hydroxide particle was covered. Or these powder was decomposed thermally at 125–150 degrees C, and the particle front face was used as the oxide. In this way, the nickel hydroxide active material concerning this invention was obtained. After mixing 1 cobalt–oxide powder eight to 10% of the weight to the nickel hydroxide powder of these various kinds and considering as the shape of a paste with the thickening liquid of CMC, the nickel fiber porous body substrate of about 95% of porosity was filled up with the specified quantity, desiccation and pressurization of were done, and the nickel electrode of this invention was produced. Moreover, the nickel electrode which does not cover the front face of a nickel hydroxide particle was made into the example of a comparison. Since densification of the powder itself was carried out when the nickel hydroxide powder which carried out dissolution liquid addition of zinc and the cobalt at the maximum was used, the energy density of this invention electrode is nickel2 per unit weight of an active material (OH). The decrement of capacity was offset by increase of a fill, and there is no substantial fall and it secured 500 mAh/more than cc.

[0012] In order to investigate charging efficiency, a potential property, etc. in each temperature of these nickel electrode, the open type cel was constituted through the separator by having made the cadmium electrode into the partner pole, and charge and discharge were performed in the electrolytic solution which made the potassium hydroxide the subject. Charge carried out discharge to to 0V to the mercury–oxide reference electrode to 150% with the rate of 0.2C at the rate of 0.1C. The average oxidation potential  $V_{ox}$  and oxygen evolution potential  $V_{o2}$  of a typical nickel electrode And the relation of the potential difference  $\eta$  is shown in drawing 1 . In addition, the potential difference  $\eta$  was made into the standard of an oxygen overvoltage. The potential difference  $\eta$  when charging the nickel electrode using various kinds of above–mentioned nickel hydroxide powder at various temperature and the relation of an active material utilization factor are shown in drawing 2 . An active material utilization factor is correlated with the potential difference  $\eta$ , and it turns out that it increases in proportion to the potential difference  $\eta$ . That is, that what is necessary is just to enlarge the potential difference  $\eta$  by making oxygen evolution potential into \*\* and making oxidation potential into \*\*, in order to raise the charging efficiency of a nickel electrode, if the potential difference  $\eta$  in the charge temperature is 20mV or more (on the right of the dotted line of drawing 2 ), it turns out that 80% or more of charging efficiency (active material utilization factor) becomes possible.

[0013] Oxidation potential  $V_{ox}$  and oxygen evolution potential  $V_{o2}$  with an ambient temperature of 20 degrees C when changing the content of the cobalt in nickel hydroxide powder about the electrode and the example of a comparison of said this invention It investigated. The relation is shown in drawing 3 . The cobalt which carried out solid–solution addition has the operation which shifts the oxidation potential of a nickel electrode to \*\*, and it turns out that the potential

difference  $\eta$  increases in proportion to the amount of cobalt. On the other hand, it is the oxygen evolution potential  $V_{O2}$ . Although it hardly changed with the amounts of cobalt, it shifted to \*\* by covering the compound of zinc, magnesium, copper, silver, an indium, a lanthanum, lead, or a scandium on the front face of nickel hydroxide powder. This covering does not necessarily need to be the whole front face, and that amount has 1 – 8 desirable % of the weight to the viewpoint of the high-rate-discharge engine performance or energy density to nickel hydroxide powder.

[0014] Drawing 4 is the example of a comparison which made 0% the content of the cobalt in nickel hydroxide powder, and oxidation potential  $V_{ox}$  and the oxygen evolution potential  $V_{O2}$ . Change is shown. [ in / electrodes / A and B / which were made into% / 5 / and 10% / this invention / the charge temperature of 5–60 degrees C ] Moreover, change of the oxygen evolution potential when changing the addition of LiOH to the electrolytic solution in the charge temperature of 60 degrees C about this invention electrode A is shown in drawing 4 . In the nickel electrode which is a semiconductor electrode, although the temperature dependence of the oxidation potential  $V_{ox}$  is small, in order to shift to \*\* greatly in connection with a temperature rise, it turns out that the potential difference  $\eta$  became small and the oxygen evolution potential  $V_{O2}$  has produced decline in the charging efficiency in an elevated temperature. Although there is no shift to \*\* of oxidation potential  $V_{ox}$ , the 60 degrees C [ of elevated temperatures ] potential difference  $\eta$  serves as zero and it will be in the condition of an oxygen evolution reaction having priority and hardly charging, in the example of a comparison since cobalt is not contained In this invention electrodes A and B which contained cobalt 5% of the weight or more, and covered the compound of zinc, magnesium, lead, silver, copper, a lanthanum, an indium, or a scandium, the potential difference  $\eta$  20mV or more was acquired in this \*\*, and 80% or more of charging efficiency became possible.

[0015] Moreover, the spark test was performed, combining this invention electrode and the KOH electrolytic solution (specific gravity 1.28–1.30) which added the lithium hydroxide, as shown in Table 1. The result is shown in drawing 5 .

[0016]

[Table 1]

電池の種類	電極の種類	電解液へのLiOHの添加量 (モル/リットル)
イ	本発明電極	0
ロ	同上	1
ハ	同上	1.5
ニ	比較例	0
ホ	同上	1.5

[0017] It became the thing excellent in the charging efficiency further in an elevated temperature so that the discharge property of drawing 5 might see. This is because the lithium of the electrolytic solution has a shift \*\*\*\* operation for oxygen evolution potential in \*\* more as shown in drawing 4 . It is 1.5 mols/l. conventionally. One mol/l. of the range which does not produce these problems among cell I using this invention electrode, RO, and Ha although disappearance of electrical-potential-difference surface smoothness, the fall of a low-temperature discharge property, etc. were produced since addition of the above high-concentration lithium was needed It turns out that the discharge property excellent in cell RO of the following lithium additions is shown. drawing 6

becomes the zinc to nickel hydroxide and the solid-solution addition of cobalt, and the cause of electrode swelling -- low -- the relation of the yield of consistency  $\gamma$ -NiOOH is shown. By addition of cobalt, generation of  $\gamma$ -NiOOH is not controlled but the prevention understands that coexistence in the zincky dissolution condition is indispensable for it. In addition, magnesium also has equivalent effectiveness.

[0018]

[Effect of the Invention] As mentioned above, according to this invention, since the nickel [ which is excellent in the charging efficiency at the time of an elevated temperature ] electrode for alkaline batteries pollution-free by the high energy consistency long lasting by which electrode swelling was prevented, and the alkaline battery using it can be offered, the industrial value is size very much.

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DESCRIPTION OF DRAWINGS

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[Brief Description of the Drawings]

[Drawing 1] The typical charging curve Fig. of a nickel electrode

[Drawing 2] The graph which shows the active material utilization factor of a nickel electrode, and relation with the potential difference  $\eta$

[Drawing 3] The graph which shows the relation between this invention electrode, the cobalt content in the example of a comparison, and charge potential

[Drawing 4] The temperature variation diagram of this invention electrode, the oxidation potential of the example of a comparison, and oxygen evolution potential

[Drawing 5] The graph which shows change of the charge potential of this invention electrode when changing the discharge property of this invention electrode and the example of a comparison, and the lithium addition to the electrolytic solution

[Drawing 6] The graph which shows the yield of gamma-NiOOH accompanying change of the zinc to nickel hydroxide, and the content of cobalt

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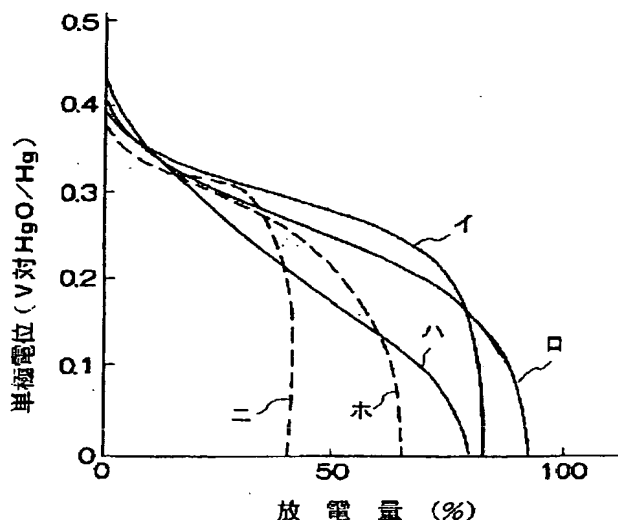
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(54) 【発明の名称】 アルカリ蓄電池用ニッケル電極とこれを用いたアルカリ蓄電池

(57) 【要約】

【目的】 電極膨潤を防止した長寿命で、且つ高温時の充電高率の優れたアルカリ蓄電池用ニッケル電極とこれを用いたアルカリ蓄電池を提供する。

【構成】 正極の主活物質である水酸化ニッケル粉末に亜鉛、マグネシウムおよびコバルトを固溶状態で含有し、かつ該水酸化ニッケル粉末を亜鉛、マグネシウム、鉛、インジウム、銀、銅、ランタンまたはスカンジウム化合物で被覆したことを特徴とするアルカリ蓄電池用ニッケル電極と、この電極と1モル/リットル以下の水酸化リチウムを添加したアルカリ電解液とを組み合わせたアルカリ蓄電池。



## 【特許請求の範囲】

【請求項1】 正極の主活物質である水酸化ニッケル粉末に亜鉛、マグネシウムおよびコバルトを固溶状態で含有し、かつ該水酸化ニッケル粉末を亜鉛、マグネシウム、鉛、インジウム、銀、銅、ランタンまたはスカンジウムの化合物で被覆したことを特徴とするアルカリ蓄電池用ニッケル電極。

【請求項2】 前記の水酸化ニッケル粉末の内部細孔容積が0.1 ml/g 以下で、その粒子形態が球状であり、コバルトの含有量が5重量%以上である請求項1記載のアルカリ蓄電池用ニッケル電極。

【請求項3】 前記水酸化ニッケル粉末を被覆する化合物が水酸化物あるいは酸化物であり、その被覆量が水酸化ニッケルに対して1～8重量%である請求項1記載のアルカリ蓄電池用ニッケル電極。

【請求項4】 請求項1記載のニッケル電極と1モル/l以下の水酸化リチウムを添加したアルカリ電解液とを組み合わせ用いることを特徴とするアルカリ蓄電池。

## 【発明の詳細な説明】

## 【0001】

【産業上の利用分野】本発明は、ニッケル・カドミウム蓄電池やニッケル金属水素化物蓄電池等に用いられるアルカリ蓄電池用ニッケル電極とこれを用いたアルカリ蓄電池に関するものである。

## 【0002】

【従来の技術】ニッケル・カドミウム電池、ニッケル金属水素化物電池は、ポータブルエレクトロニクス機器等の携帯電源として幅広く使用されているが、年々これら機器の小型軽量化に伴い、これら機器内に収納されて使用される電池の作動雰囲気は高温となる傾向にある。このため、これら電池の高温特性の改良、特に充電効率の向上が強く要求されている。また近年電気自動車用電源としてこれら電池が注目されているが、使用環境が炎天下での走行や駐車であり、電池周囲温度が60℃前後となるため、高温時の充電効率の向上は不可欠となっている。

【0003】従来、電池の高温時の充電効率の向上には、水酸化ニッケル電極の酸化反応と競合する酸素発生反応を抑制するために、電解液の分解電位を上げたりニッケル電極自体の酸素過電圧を高めることが行われている。具体的には、①電解液である水酸化カリウム水溶液に高濃度の水酸化リチウムを添加する方法、②主活物質である水酸化ニッケルにコバルトを固溶体添加する方法、③水酸化ニッケルの表面を水酸化カドミウムで被覆する方法等が行われている。

【0004】しかしながら、①の方法は、電解液の抵抗を増し、低温高率放電特性の低下や容量の劣化、電圧の平坦性の消失等を伴い、しかもこの方法のみで40℃以上の高温領域にて優れた充電効率を得るには限界があった。②の方法は、コバルトを多量添加することによって

高温性能の向上を可能とするが、活物質の単位重量当りの容量の減少や電極膨潤による寿命の低下等を生じる。また、③の方法は、酸素発生電位を貴にして酸素過電圧を向上させるが、カドミウムは高温充電時に電解液中に一部溶出して負極に析出し短絡を生じる可能性を持ち、①と同様にこの方法のみで40℃以上の高温領域にて優れた充電効率を得るには限界があった。このように従来の方法には問題点があり、上述の要求を十分に満足するに至っていない。

## 【0005】

【発明が解決しようとする課題】本発明は上記問題点を鑑みてなされたものであり、電極膨潤を防止した長寿命で、かつ電極のエネルギー密度を減少させることなく、高温時の充電効率の優れたアルカリ蓄電池用ニッケル電極と該電極を用いたアルカリ蓄電池を提供するものである。

## 【0006】

【課題を解決するための手段】本発明のニッケル電極は、主活物質である水酸化ニッケル粉末として、亜鉛、マグネシウムとコバルトを固溶状態で含有し、水酸化ニッケル粒子を亜鉛、マグネシウム、鉛、インジウム、銀、銅、ランタンまたはスカンジウムの化合物で表面被覆した粉末を用いたことを特徴とし、水酸化ニッケル粒子は内部細孔容積が0.1 ml/g 以下で球状形態であることが望ましく、水酸化ニッケル粉末のコバルト含有量は5～10重量%であり、前記化合物の被覆量は水酸化ニッケルに対して1～8重量%であることが好ましい。また、本発明のアルカリ蓄電池は、上記ニッケル電極と1モル/l以下の水酸化リチウムを添加したアルカリ電解液とからなることを特徴とする。

## 【0007】

【作用】ニッケル電極の充電効率は、競合反応である酸素発生反応（電解液の分解反応）を抑制することによって向上する。この酸素発生反応は、水酸化ニッケル活物質の酸化電位をより卑に、酸素発生電位をより貴にして、酸素過電圧（酸素発生電位と酸化電位の差）をより大きくすることによって抑制可能となる。水酸化ニッケルへのコバルトの固溶体添加は、その量に比例してニッケル電極の酸化電位を卑にする作用をもつ。また、亜鉛、マグネシウムを同時に固溶体添加することによって、ニッケル電極の膨潤の原因であるγ-Ni(OH)の生成が防止されて長寿命化を可能にする。コバルトの単独添加ではこの作用はない。また、コバルトの多量添加による活物質の単位重量当りの容量減少による電極のエネルギー密度の低下は、水酸化ニッケル粉末の内部細孔容積を従来製法の粉末より小さくして高密度化し、かつその形状を球状として粉末自体のタッピング密度を上げることによって防止することが可能となる。

【0008】一方、酸素発生電位の貴へのシフトは、固溶体添加した亜鉛によっても生じるが、酸素発生反応の

場である水酸化ニッケル粒子の表面に亜鉛、マグネシウム、鉛、インジウム、銀、銅、ランタンまたはスカンジウムの化合物を被覆することによって、より効果的に行わせることが可能となる。特に、該元素が亜鉛、マグネシウム、鉛、ランタン、インジウムまたはスカンジウムである場合には、たとえ被覆した化合物が電解液中に一部溶解したとしても、カドミウム電極や金属水素化物電極の充放電電位では金属として析出することではなく、従来法の水酸化カドミウム被覆の場合のように負極に析出して短絡等を生じる可能性がなくなる。また、本発明の酸素過電圧の高い活物質のニッケル電極への適用と、電圧の平坦性や低温時の放電特性の劣化を伴わない範囲の低濃度の水酸化リチウムの電解液への添加との組み合わせによって、更に高温時の充電効率および放電特性の優れたアルカリ蓄電池を構成することが可能となる。

【0009】このように本発明は、ニッケル電極の酸化電位と酸素発生電位との電位差を顕著に増大させて高温時の充電効率を高めると共に、電極膨潤を抑制した無公害のニッケル電極を得ることを可能とする。

【0010】

【実施例】本発明の実施例の詳細を以下に述べる。本発明の水酸化ニッケル粉末は、硫酸ニッケルに硫酸亜鉛あるいは硫酸マグネシウムと硫酸コバルトの所定量を加えた水溶液に、硫酸アンモニウムを添加してアンミン錯体とし、アルカリ度をpH11～13に制御しながら、水酸化ナトリウム水溶液を激しく攪拌しながら滴下し、亜鉛、マグネシウムとコバルトの含有量の異なる各種の水酸化ニッケル粒子を析出成長させて作製した。亜鉛、マグネシウムおよびコバルトの含有量はそれぞれ0～8重量%と0～10重量%の範囲で調製した。得られた水酸化ニッケル粉末のタップ密度は約2g/ml、窒素吸着法で測定した内部細孔容積は0.02～0.09ml/g、その形態は球状であり、公知の従来法により作製した粉末(タップ密度は1.6g/ml、内部細孔容積は0.14ml/g)に比較して約20%高密度な粉末であった。

【0011】これら粉末を、一定量の硫酸亜鉛、硫酸カドミウム、硫酸銅などの水溶液に浸漬した後に、水酸化ナトリウム水溶液に浸漬して水酸化物とし、水酸化ニッケル粒子の表面を被覆した。あるいは、これら粉末を125～150℃にて加熱分解し、粒子表面を酸化物とした。こうして本発明に係る水酸化ニッケル活物質を得た。これら各種の水酸化ニッケル粉末に一酸化コバルト粉末を8～10重量%混合し、CMCの増粘液にてペースト状とした後に、約95%の多孔度のニッケル繊維多孔体基板に所定量を充填して、乾燥・加圧し本発明のニッケル電極を作製した。また、水酸化ニッケル粒子の表面を被覆しないニッケル電極を比較例とした。本発明電極のエネルギー密度は、亜鉛およびコバルトを最大限に固溶液体添加した水酸化ニッケル粉末を用いた場合においても、粉末自体が高密度化されたために、活物質の単

位重量当りのNi(OH)<sub>2</sub>容量の減少分は充填量の増大によって相殺され、実質的な低下はなく、500mAh/cc以上を確保した。

【0012】これらニッケル電極の各温度での充電効率や電位特性等を調べるために、カドミウム電極を相手極としてセパレーターを介して開放形セルを構成し、水酸化カリウムを主体とした電解液中で充放電を行った。充電は0.1C率で150%、放電は0.2C率で酸化水銀参照電極に対して0Vまでとした。典型的なニッケル電極の平均酸化電位 $V_{ox}$ 、酸素発生電位 $V_{o_2}$ およびその電位差 $\eta$ の関係を図1に示す。尚、電位差 $\eta$ を酸素過電圧の目安とした。上記の各種の水酸化ニッケル粉末を用いたニッケル電極をいろいろな温度で充電した時の電位差 $\eta$ と活物質利用率の関係を図2に示す。活物質利用率は電位差 $\eta$ と相関し、電位差 $\eta$ に比例して増加するのがわかる。すなわち、ニッケル電極の充電効率を向上させるには、酸素発生電位を貴にし酸化電位を卑にすることで電位差 $\eta$ を大きくすれば良く、その充電温度での電位差 $\eta$ が20mV以上(図2の点線より右側)であれば、80%以上の充電効率(活物質利用率)が可能となるのがわかる。

【0013】前記本発明の電極と比較例について、水酸化ニッケル粉末中のコバルトの含有量を変化させた時の周囲温度20℃での酸化電位 $V_{ox}$ と酸素発生電位 $V_{o_2}$ を調査した。その関係を図3に示す。固溶体添加したコバルトは、ニッケル電極の酸化電位を卑にシフトさせる作用があり、電位差 $\eta$ はコバルト量に比例して増大するのがわかる。一方、酸素発生電位 $V_{o_2}$ はコバルト量によって殆ど変化しないが、亜鉛、マグネシウム、銅、銀、インジウム、ランタン、鉛またはスカンジウムの化合物を水酸化ニッケル粉末の表面に被覆することによって貴にシフトした。この被覆は必ずしも表面全体である必要はなく、その量は高率放電性能やエネルギー密度の観点から、水酸化ニッケル粉末に対して1～8重量%が望ましい。

【0014】図4は、水酸化ニッケル粉末中のコバルトの含有量を0%とした比較例と、5%、10%とした本発明電極A、Bについて、充電温度5～60℃における酸化電位 $V_{ox}$ および酸素発生電位 $V_{o_2}$ の変化を示したものである。また、図4には、本発明電極Aについて、充電温度60℃において電解液へのLiOHの添加量を変化させた時の酸素発生電位の変化を示してある。半導体電極であるニッケル電極では、その酸化電位 $V_{ox}$ の温度依存性は小さいが、酸素発生電位 $V_{o_2}$ は温度上昇に伴い大きく卑にシフトするために、電位差 $\eta$ が小さくなって高温での充電効率の低下を生じているのがわかる。比較例では、コバルトを含有していないので酸化電位 $V_{ox}$ の卑へのシフトがなく、高温60℃での電位差 $\eta$ はゼロとなり、酸素発生反応が優先して殆ど充電されない状態となるが、コバルトを5重量%以上含有しか

つ亜鉛、マグネシウム、鉛、銀、銅、ランタン、インジウムまたはスカンジウムの化合物を被覆した本発明電極A、Bでは、同温にて20 mV以上の電位差 $\eta$ が得られ、80%以上の充電効率が可能となった。

【0015】また、本発明電極と水酸化リチウムを添加

したKOH電解液(比重1.28~1.30)とを表1のように組み合わせて放電試験を行った。その結果を図5に示す。

【0016】

【表1】

電池の種類	電極の種類	電解液へのLiOHの添加量(モル/リットル)
イ	本発明電極	0
ロ	同上	1
ハ	同上	1.5
ニ	比較例	0
ホ	同上	1.5

【0017】図5の放電特性に見られるように、更に高温での充電効率が優れたものとなった。これは、図4に示すように電解液のリチウムが酸素発生電位をより貴にシフトさす作用を持つためである。従来は1.5モル/l以上の高濃度のリチウムの添加を必要としたため、電圧平坦性の消失や低温放電特性の低下等を生じたが、本発明電極を用いた電池イ、ロ、ハのうちそれら問題を生じない範囲の1モル/l以下のリチウム添加量の電池ロが優れた放電特性を示すのがわかる。図6は、水酸化ニッケルへの亜鉛およびコバルトの固溶体添加量と電極膨潤の原因となる低密度な $\gamma$ -NiOOHの生成率の関係を示したものである。 $\gamma$ -NiOOHの生成はコバルトの添加では抑制されず、その防止には亜鉛の固溶状態での共存が必要不可欠であるのがわかる。尚、マグネシウムでも同等の効果がある。

【0018】

【発明の効果】上述のように本発明によれば、高温時の

充電効率に優れ、電極膨潤が防止された長寿命な、かつ高エネルギー密度で無公害なアルカリ蓄電池用ニッケル電極とそれを用いたアルカリ蓄電池を提供することができるので、その工業的価値は極めて大である。

【図面の簡単な説明】

【図1】ニッケル電極の典型的な充電曲線図

【図2】ニッケル電極の活物質利用率と電位差 $\eta$ との関係を示すグラフ

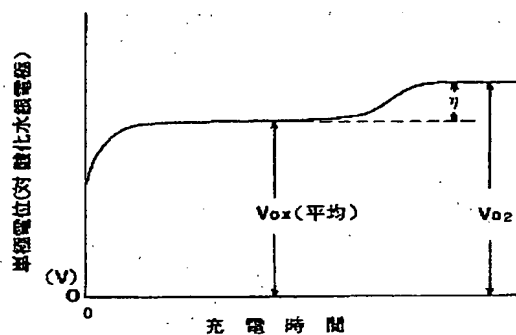
【図3】本発明電極と比較例におけるコバルト含有量と充電電位の関係を示すグラフ

【図4】本発明電極と比較例の酸化電位と酸素発生電位の温度変化図

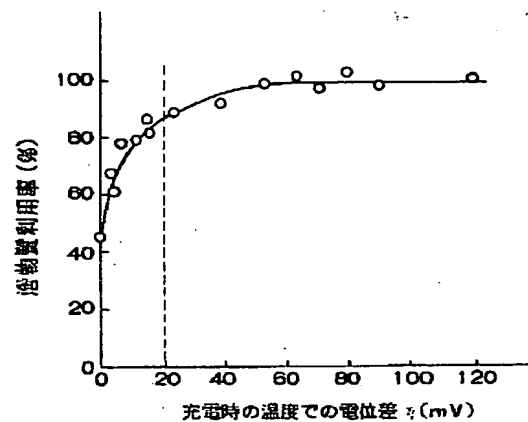
【図5】本発明電極と比較例の放電特性及び電解液へのリチウム添加量を変化させた時の本発明電極の充電電位の変化を示すグラフ

【図6】水酸化ニッケルへの亜鉛とコバルトの含有量の変化に伴う $\gamma$ -NiOOHの生成率を示すグラフ

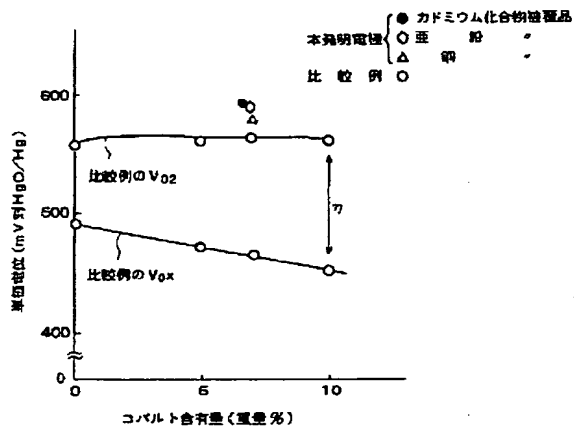
【図1】



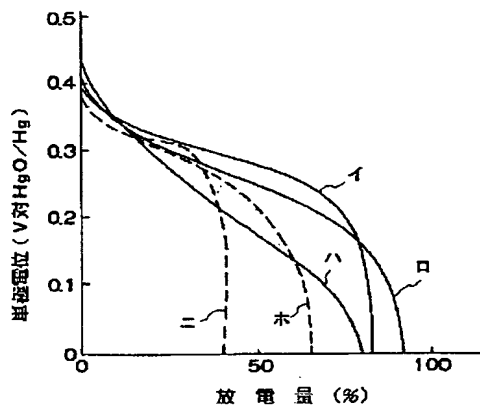
【図2】



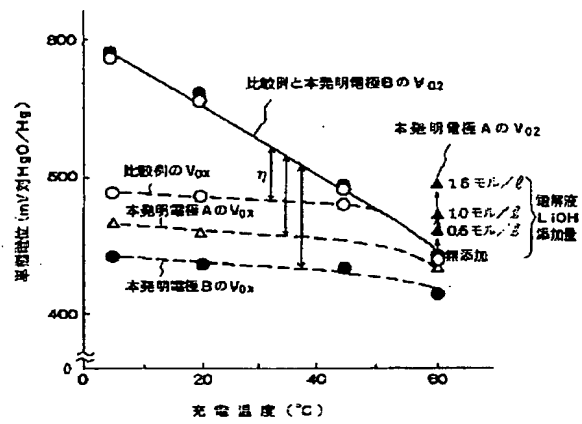
【図3】



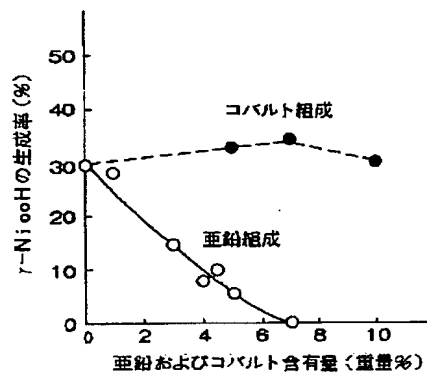
【図5】



【図4】



【図6】



フロントページの続き

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